ACIDIC LAKES IN ONTARIO: CHARACTERIZATION, EXTENT, AND RESPONSES TO BASE AND NUTRIENT ADDITIONS

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ACIDIC LAKES IN ONTARIO:

CHARACTERIZATION, EXTENT, AND RESPONSES

TO BASE AND NUTRIENT ADDITIONS

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PREFACE

The Sudbury Environmental Study was initiated in 1973 in part to determine the geographical extent of acidic lakes in the area of Sudbury, Ontario, to characterize the chemical and biological nature of lakes stressed by elevated acid and metal levels, and to determine the chemical and biological response of the acidified lakes to base additions.

This report, prepared for and presented at the "Jubilee Symposium on Lake Metabolism and Lake Management" held at Uppsala University in Sweden in August 1977, presents an overview of major results obtained to date by the Limnology Unit of the Water Resources Branch and the Technical Support Group (Water Resources) of the Northeastern Region. As such, it includes data collected from 1973 to 1976. Some information collected as part of the Lakeshore Capacity Study is also presented.

TABLE OF CONTENTS

	Page
PREFACE	i
TABLE OF CONTENTS	ii
INTRODUCTION	1
METHODS	2
RESULTS AND DISCUSSION	2
A. Precipitation Chemistry	2
B. Synoptic Lake Surveys	5
C. Intensive Studies	6
i. Chemistry and Biology of an Acidic Lake	6
ii. Effects of base additions	19
iii. Effects of phosphorus additions	24
SUMMARY	29
REFERENCES	31
LIST OF FIGURES	20

INTRODUCTION

The study of acid precipitation and its effects on aquatic ecosystems in Canada has been almost wholly centred on the greater Sudbury area of the Province of Ontario. This emphasis is not surprising since the nickel smelting industries in Sudbury have emitted between 1.5 and 2.7×10^6 m.t. of 80^2 yr⁻¹ for a minimum of 25 years (Fig. 1) and the airborne conversion of 80^2 to sulphuric acid is well documented (Brosset 1973, Lusis and Wiebe 1976). In fact, emissions from a single 381 m. high stack operating since 1972 represent the world's single largest point source of 80^2 (Summers and Whelpdale 1975) with an estimated output of 3.1×10^6 kg day 1 . Heavy metal emissions in the Sudbury area, amounting to an estimated 2200 m.t. Fe yr⁻¹, 1100 m.t. Ni yr⁻¹ and 1100 m.t. Cu⁻¹ (Air Resources Branch, Ontario Ministry of the Environment) are also of great concern.

It is well known that acidic precipitation and heavy metal deposition have severely affected both terrestrial and aquatic ecosystems in the greater Sudbury area. Damage to plants and soils by SO_2 and its oxidation product H_2SO_4 has been documented (Linzon 1972; Gorham and Gordon 1960a, b; McGovern and Balsillie 1973; Hutchinson and Whitby 1973) and the detrimental effects on phytoplankton (Stokes et al. 1963; Yan and Stokes 1976; Kwiatkowski and Roff 1976), zooplankton (Sprules 1975), macrophytes (Gorham and Gordon 1963) and fish (Ontario Water Resources Commission 1971; Beamish and Harvey 1972; Beamish 1974, 1976; Beamish et al. 1975) have been shown both in the immediate vicinity of Sudbury and in the La Cloche Mountains, 65 km to the SW. Recently, evidence has been accumulating which indicates that serious environmental problems resulting from the airborne transport of contaminants are widespread in southern Ontario (Dillon et al. 1977).

This paper outlines the extent of this phenomenon in Ontario and summarizes investigations into the effects of base and nutrient additions

on the chemistry and biota of selected acidic lakes.

METHODS

Methods of precipitation sampling are described in Dillon <u>et al</u> (1977). Base and nutrient addition techniques, lake and stream sampling and analytical techniques are described in Scheider <u>et al</u> (1975, 1976). Conroy <u>et al</u> (1975) summarize methods of the synoptic lake sampling.

RESULTS AND DISCUSSION

A. Precipitation Chemistry

The range in mean pH of bulk precipitation collected at six sites near Sudbury in 1976 was 4.2 to 4.5, amounting to a free H^{+} deposition of 60 to 30 meq $m^{-2}yr^{-1}$ (Table 1). There was no apparent relation with distance from the 381 m stack. Beamish and Van Loon (1977) measured similar H^{+} deposition and pH in the La Cloche Mountains, 65 km SW of Sudbury. The present pH of precipitation in Sudbury is very similar to that in S. Norway (Dovland, Joranger and Semb 1976) and in Sweden (Oden 1976) while it is still 0.1 to 0.3 pH units less acid than that reported for the NE USA (Likens 1976).

Kramer (1976a) monitored bulk precipitation in the Sudbury area from 1970-1975 and showed that the chemistry of the precipitaton changed in 1972. His results for 1973-1975 were similar to those we measured in 1976. However, in 1972 the 381 m stack replaced three smaller chimneys, increased removal of particulates was implemented, and emissions of SO_2 were reduced by 35%. Although this resulted in a decrease of mean sulphate deposition, H^+ deposition increased by 60% at ten precipitation collection sites with pre- and post-1972 data.

Table 1. Mean and range for pH, SO₄ deposition, and heavy metal deposition rates as measured by bulk collectors for 6 stations near Sudbury, Ontario, in 1976.

	Location from	р	Н		Deposition	on (g m	2yr ⁻¹)	
Station	Sudbury	mean ^a	range	SO ₄	Cu	Ni	Zn	Fe
Kelly Lake	3 km SE	4.43	4.0-4.9	8.1	0.36	0.13	0.28	0.23
Hannah Lake	4 km SE	4.20	3.9-4.8	5.8	0.24	0.091	0.057	0.41
Middle Lake	5 km SE	4.33	3.9-6.3	7.4	0.20	0.14	0.13	0.29
Lohi Lake	10 km SE	4.21	3.8-4.5	5.3	0.18	0.050	0.10	0.12
Nelson Lake	30 km N	4.54	4.2-5.8	3.2	0.080	0.008	0.09	0.050
Mountaintop Lake	50 km N	4.33	4.2-4.9	3.7	0.021	0.009	0.10	0.045

1 1 1 1

 $^{^{}a}$ calculated as volume-weighted arithmetic mean of hydrogen ion concentration (eq 1^{-1}) converted to its negative logarithm.

Annual metal and SO₄ deposition rates for the Sudbury area were calculated for 1976 (Table 1). Loading rates of Cu, Ni, Zn and Fe were extremely high compared to other areas receiving acidic precipitation (Henriksen 1972) and were correlated strongly with distance from the source of emissions. The sulphate deposition rates indicated that of the order of 1% of the total emissions were deposited as SO₄ within a 4000 km² area surrounding Sudbury. The fact that such a small percentage of SO₂ emissions were deposited in this large area is supported by the low oxidation rate of about 1% hr⁻¹ measured in the plume (Lusis and Wiebe 1976). Thus, the long-range transport of the emitted gases is certain.

To ascertain the extent of acid rain in south-central Ontario, we began operation of a network of precipitation collectors in 1976. The range in mean pH of bulk precipitation samples from 8 sites located on the Precambrian Shield (Fig. 2) was 3.95 to 4.22, identical to values measured by Likens et al (1976) in the NE USA, lower than reported for Scandinavia (Dovland, Joranger and Semb 1976, Odén 1976) and lower than indicated by our Sudbury data. In fact, the overall mean [H⁺] was 50% greater in south-central Ontario than in the Sudbury area. Stations located on calcareous areas on the boundary of the Shield had higher mean pH because entrained material was capable of buffering the precipitation.

The source of the acidity in precipitation in this region is not yet clear. Major industrial sources of SO_2 are located to the NW and N of the study area and long range transport is such that these sources may impact on south-central Ontario. However, Lafleur and

Whelpdale (1977) have shown that high atmospheric sulphate levels in S. Ontario are associated with air masses moving from the south and southwest. It is likely that no one source can be pinpointed, but rather that the problem of acid rain is one of massive scale throughout eastern North America.

Much of the Precambrian Shield is formed of plutonic bedrock composed primarily of granite, granite gneiss, granite pegmatite and migmatite. The overburden consists almost exclusively of shallow till, often <1 m in depth, of acidic podzols. Exposed bedrock is found frequently. The freshwater of a major portion of eastern Canada is therefore poorly buffered (Fig. 3). Continued inputs of acidic precipitation to these areas will result in extensive acidification of many lakes and streams (Kramer 1976b, 1976c). The rate at which this will occur in each one of the hundreds of thousands of water bodies depends almost wholly on the rather small buffering capacity of the very thin layer of overburden in each watershed.

B. Synoptic Lake Surveys

To determine the extent of lakes affected by the elevated H⁺, sulphate and metal depositions, 209 lakes within a 200 km radius of Sudbury were investigated between 1974 and 1976. Lakewater sulphate levels (Fig. 4b) were found to be higher NE and SW of Sudbury, a pattern that corresponded closely with prevailing wind directions (Fig. 4c). Although lake pH showed a generally similar trend (Fig. 4a) there were many more irregularities caused by local differences in bedrock and surficial geology and hence in buffering capacity of watersheds. Many of the most severely affected lakes are situated in quartzite rock with virtually no overburden, while others, some very close to Sudbury, have sufficient calcareous deposits to ensure adequate buffering capacity.

The effects of low pH on fish have received particular attention in several parts of the world (Schofield 1976, Leivestad et al 1976, Beamish and Harvey 1972). It is generally accepted (EIFAC 1969) that a pH of at least 5.5 is necessary for the reproductive success of some fish species, particularly salmonids. The zone of lakes near Sudbury with pH <5.5, which includes about 5300 km², is notable for the scarcity of lakes with remaining trout populations (Figure 4d). A few lakes of depressed pH retain trout populations (Fig. 4e); these are, however, probably disappearing. The distribution of nickel and copper in surface waters and lake sediments (Fig. 5) showed elevated levels in an area surrounding the smelting complex. Because nickel levels are high in the smelter emissions but naturally low in lakes, nickel serves as a useful indicator of airborne contamination. Of course, depressed pH is instrumental in maintaining high concentrations of soluble copper and nickel in the water column.

Recently, indications of heavy metal contamination in areas remote from Sudbury have become evident (Table 2). Lakes in south-central Ontario have Cu, Ni, Zn and Mn levels that are substantially greater than those of unaffected lakes in N.W. Ontario (Beamish 1976). Metal levels already approach or exceed those found in lakes in the La Cloche Mountains, 65 km SW of Sudbury (Beamish 1976).

C. Intensive Studies

i. Chemistry and Biology of an Acidic Lake

In 1973, intensive studies of four lakes in the vicinity of Sudbury were initiated (Fig. 6). Our goals were: a) to investigate the chemical and biological nature of lakes stressed by elevated acid and metal levels; b) to determine the effects of base additions on the lake chemistry and biota; c) to study lake responses to other stresses, notably nutrient

Table 2. Heavy metal concentrations in lake waters. Data for SE Norway are from Wright and Gjessing (1976), La Cloche and ELA lakes data from Beamish (1976).

Lake region	-	Cu	Ni (mg	Zn m ⁻³)	Mn
SE Norway		1-10	-	3-35	 .
La Cloche mountain	ıs - 4 lakes	2-4	8-12	24-36	220-260
ELA (NW Ontario) -	102 lakes	2	<3	<1	3
South-central Ontario	14 lakes	5.7	3.6	12.6	49

additions. An additional four lakes are presently under investigation and substance budgets are being monitored for all lakes. Information on drainage basin geology, lake morphometry and type of treatment for 5 lakes is summarized in Table 3.

To characterize a typical acid and metal-stressed lake in the Sudbury area and to underscore the effects of base and nutrient additions on other lakes, Clearwater Lake has been investigated as a control since 1973. The lake is thermally dimictic, clear (mean Secchi transparency 8-11m) with a welloxygenated hypolimnion ($[0_2]$ >7 mg 1^{-1}). Major ion chemistry is summarized in Table 4 and compared to unaffected lakes in NW Ontario (ELA) and south-central Ontario (Blue Chalk Lake). The latter two have similar ionic chemistry, with Ca and SO4 levels in Blue Chalk Lake somewhat higher. This perhaps reflects the recent acid rain phenomenon previously described. Clearwater Lake, however, had significantly elevated levels of Ca, Mg, Na and K due to the substitution of H from precipitation for cations in the overburden of the watershed during runoff (Likens and Bormann 1975, Schindler et al 1976, Henriksen and Wright 1976). Lake SO4 levels were also high (26 mg 1⁻¹). Compared to acidic lakes in Norway and Sweden (Wright and Gjessing 1976), Clearwater Lake showed elevated concentrations of Ca, SO4 and, to a lesser extent, Mg.

Levels of SO₄ in Clearwater Lake were approximately in equilibrium with those in incoming runoff. By employing an areal unit runoff figure of 0.6 m yr $^{-1}$ (Pentland 1968) and the measured annual input of SO₄ from precipitation (5 g m $^{-2}$), it was calculated that lakewater SO₄ should be about 1/3 of actual measured values. This implies that direct input of SO₂ - SO₄ via fumigation of particulate material is the most important SO₄ source (Benarie 1976). Less probable sources are the leaching of vegetation

Table 3. Drainage basin geology, lake surface area (A_0) , mean depth (\bar{z}) , drainage basin area (A_d) , flushing rate (ρ) and type of treatment applied to six study lakes (P = phosphorus addition).

Lake	Bedrock geology	Ao	ž	A _d ¹	ρ		Tre	atment	
		(km²)	(m)	(km²)	(yr ⁻¹)	1973	1974	1975	1976
Clearwater	gneiss, migmatite, quartzite	0.72	8.1	3.2	0.40	-	-	=:	-
Lohi	quartzite, gabbro	0.40	6.2	4.7	1.2	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂ + CaCO ₃	-
Hannah	quartzite	0.21	4.0	0.94	0.81	•	-	Ca(OH) ₂ + CaCO ₃	Р
Middle	quartzite, gabbro	0.30	6.2	2.6	0.95	Ca(OH) ₂ + CaCO ₃	-	Р	Р
Nelson	granophyre, volcanic breccia	3.09	11.6	8.0	0.19	-	2	Ca(OH) ₂ + CaCO ₃	Ca(OH) ₂ ·CaCO ₃

¹excludes lake area.

Table 4. pH, conductivity and major ion content of Clearwater Lake (1973-76) compared to non-acidified lakes in the Experimental Lakes Area, Ontario (Armstrong and Schindler 1971), and on the Precambrian Shield in central Ontario (Blue Chalk Lake - Dillon et al unpub.) and to acidified lakes in southern Norway and west-central Sweden (Hörnström et al in Wright and Gjessing 1976).

		Clearw	ater		ELA	ELA Blue Chalk Lake	S. Norway	W.C. Swede
	1973	1974	1975	1976				
cond (pmho cm ⁻¹)	911	86¹	. 86¹	871	19¹	301	272	472
pΗ	4.33	4.24	4.33	4.24	5.6-6.7	6.6	4.76	4.66
				µеq] ⁻¹			
Н	46	57	46	58	<3	<1	18	22
Ca	309	277	269	294	80	140	55	75
Mg	189	96	90	140	74	70	41	80
Na	70	64	67	57	39	37	70	165
<u> </u>	_34	26	20	19	10	9	5	15
E ⁺	650	521	494	570	203	256	189	360
504	581	533	518	541	62	156	100	200
21	41	33	40	51	39	13	71	170
NO 3	8	4	4	4	< 7	<1	4	19
HCO3	0	0	0	0	62	125	_11	
-	630	570	562	596	164	294	186	390

¹at 25°C

²at 20°C

Table 5. Heavy metal concentrations (mg m^{-3}) in Clearwater Lake and Blue Chalk Lake (south-central Ontario).

	1973	Clear 1974	water 1975	1976	Blue Chalk Lake
Cu	90	97	110	92	8
free Cu	-	-	61	88	-
Ni	270	290	270	270	3
Zn	40	47	48	50	9
free Zn	æ	-	42	38	-
A1	-	520	440	400	13
Mn	-	310	290	300	40
Fe	110	100	130	100	41

and the weathering of the overburden.

Clearwater Lake also exhibited high heavy metal levels (Table 5).

Cu, Ni, Zn, Al and Mn were all an order of magnitude greater in concentration than in lakes in south-central Ontario. A major portion of the Cu and Zn were in the "free" ionic state due to the low pH.

Sediment profiles of pH, Cu and Ni in Clearwater Lake (Fig. 7) reflect the changes in lakewater chemistry brought about by acid and metal loadings. Although the patterns are complicated by intralake variation and possible sediment mixing, gradual increases in Cu, Ni and acid are evident. Cu and Ni levels in the more recent layers were 1-3 orders of magnitude greater than in other relatively unaffected lakes in southcentral Ontario.

Nutrient levels in Clearwater Lake were similar to those of typical oligotrophic Precambrian Shield lakes in Ontario (Dillon and Rigler 1974a, Scheider and Rigler 1977). Mean annual total phosphorus concentrations were 3 to 5 mg m⁻³ while total nitrogen levels were in the 150 - 200 mg m⁻³ range (Fig. 8). Ratios of N:P for acidic lakes in the Sudbury area are generally 30 to 100 indicating that phosphorus is the nutrient in shortest supply (Schindler 1977). The fact that inorganic N (NO₃ and NH₃) was not depleted at any time over a 4 year period in Clearwater Lake also indicated that N levels were in excess.

The biota of Clearwater Lake were in some aspects quantitatively and qualitatively different from those of circumneutral Shield lakes.

The numbers of aerobic heterotrophic bacteria were probably low while numbers of aciduric bacteria were high. Phytoplankton biomass and productivity were normal for circumneutral lakes of the same nutrient status, but the species composition had been drastically altered by

acidification. Zooplankton communities were low in total biomass and diversity and had altered composition.

From 1973 to 1976 most of the phytoplankton biomass in Clearwater Lake was contributed by dinoflagellates (Fig. 9). Circumneutral Shield lakes, in contrast, are typically dominated by chrysomonads or chrysomonads and diatoms (Schindler and Holmgren 1971, Kling and Holmgren 1972, Nicholls 1976). Peridinium inconspicuum Lemmermann formed most of the dinoflagellate biomass in Clearwater Lake. As this species has also been reported as an important contributor to total biomass in acidic La Cloche Mountain lakes (Yan and Stokes 1976) and in surface waters of Swedish lakes (Hörnström et al 1973), it is apparently a good indicator of acidic conditions if it forms a substantial portion of the total phytoplankton biomass.

Hendrey <u>et al</u> (1976) have suggested that phytoplankton biomass is reduced by lake acidification. The data upon which this suggestion was based warrant re-examination.

Synoptic surveys of phytoplankton in acid lakes have been restricted to a limited number of samples in each lake. The communities have been sampled at one depth, either one-half the Secchi transparency (Kwiatkowski and Roff 1976) or at the surface (Almer et al 1974, Hörnström et al 1973). If integrated through the euphotic zone, tow nets have been employed (Leivestad et al 1976). These sampling techniques are unsuitable for appraising differences in biomass between lakes as they fail to account for vertical inhomogeneities in phytoplankton distribution (Schindler and Holmgren 1971, Fee 1976, Klemer 1976), for large seasonal fluctuations in total biomass (Willen 1969, Kling and Holmgren 1972, Schindler and Nighswander 1970) or, in the case of tow nets for the potentially significant

nannoplankton biomass (Kalff 1972). Collections should be spatially and temporally integrated. Data must be expressed in units of biomass (Vollenweider et al 1974), not as numbers of individuals per species (Kwiatkowski and Roff 1976), because sizes of individual organisms are very variable (Vollenweider 1969, p.19).

The mean biomass of the Clearwater Lake phytoplankton community from 1973 to 1976 is shown in Fig. 10 and Table 6 with other comparable data. The biomass in Clearwater Lake was similar to that in other circumneutral lakes. In our study lakes, in fact, mean biomass was better correlated with total phosphorus (r = 0.47, p < .01, Figure 10b) than with pH (r = .01, p > .5, Figure 10a). Despite the elevated concentrations of heavy metals and free hydrogen ion, the relationship between algal biomass and phosphorus (Sakamoto 1966, Dillon and Rigler 1974b) still exists as found in Swedish studies (Hörnström et al 1973, Almer et al 1974).

Previous evidence of reduced phytoplankton biomass in acidic lakes (Conroy et al 1975) is complicated by differing phosphorus levels. Lakes susceptible to acidification tend to be low in ionic strength, hence low in phosphorus unless artificially enriched. Thus, suggested correlations between pH and phytoplankton biomass are more readily explained by lake nutrient levels than by lake pH.

Estimates of primary production in Clearwater Lake are similar to those measured in Blue Chalk Lake, a lake of near neutral pH with similar morphometry and nutrient concentrations in south-central Ontario (Fig. 11). Hourly production in Clearwater Lake compares well with estimates for other nutrient poor lakes (Michalski et al 1973, Kerekes 1975). Hypolimnetic oxygen depletion rates in Clearwater Lake, a rough measure of whole lake productivity, are also typical of circumneutral oligotrophic lakes (Table 7).

Table 6. Total phosphorus, pH and mean phytoplankton biomass of selected acidic and non-acidic lakes with low phosphorus concentrations

T SO FIRE					
Lake		рН	T P (mg m ⁻³)	biomass ¹ (mg l ⁻¹)	Source
Clearwater	1973 1974 1975 1976	4.3 4.2 4.3 4.2	5 5 3 5	0.54 0.73 0.50 0.38	This study
Lohi	1973	4.7	6	0.46	JI II
Hannah	1973 1974	4.4	8 5	0.26 0.29	n n n
Middle	1973	4.7	7	0.41	и и
Carlyle	1973	5.1	12	0.60	Yan & Stokes (unpub. manuscript)
		mean	6.2	0.46	
Joe	1976	5.6	5	0.38	This study
Chub	1976	5.8	12	0.83	п п
Crosson	1976	5.8	12	0.67	н н
Clear	1967	6.0	7-15	~0.1	Schindler and Nighswander 1970
Nelson	1976	6.5	5	0.47	This study
239	1969	-	6	0.79	Kling and Holmgren 1972
305	1969	=	5	0.45	п
Blue Chalk	1976	6.6	8	0.33	This study
Walker	1976	6.7	8	0.40	н п
Balsam	1972	7.8	∿13 —	0.6	Nicholls 1976
		mean	8.5	0.50	

 $^{^{1}\}mathrm{phytoplankton}$ sampled through the euphotic zone at weekly or biweekly intervals.

Table 7. Areal hypolimnetic oxygen deficits in Clearwater Lake and neutral lakes in south-central Ontario.

Lake	Areal hypolimnetic oxygen deficit (mg cm ⁻² day ⁻¹)
Clearwater (1975)	0.022
Halls ¹	0.013
Boshkung ¹	0.019
Bob 1	0.023
Haliburton ¹	0.027
Blue Chalk	0.015
Red Chalk	0.021

¹data from Lasenby (1975)

Table 8. Mean number of crustacean zooplankton species per summer collection, range of mean zooplankton biomass (mg dry weight m^{-3}) per collection and lake pH for study lakes.

Lake	S	Mean number of pecies per collection	Range and mean biomass per collection	рН
Clearwater ¹	1973 1974 1975 1976	3.4 3.4 3.8 3.2	0.86-14 (5.3) 0.01-48 (14.1) 0.16-17 (4.6) 0.05-21 (9.7)	4.3 4.2 4.3 4.2
Hannah ¹	1973 1974	2.9	0.04-2.1 (0.61) 0.02-5.4 (0.81)	4.4 4.3
Middle ¹	1973	2.5	0.06-53 (9.0)	4.7
Lohi¹	1973	3.5	0.17-51 (19.9)	4.7
Nelson¹	1975 1976	8 7	25-65 (34) 20-60 (35)	5.7 6.5
E.L.A. lakes²	1968	8.4		5.6-6.7
La Cloche ³ Mountain Lakes	1971-197	3.2 8.3 10.4		3.8-4.9 5.0-5.9 6.0-7.0
Maggiore ⁴	1966-196	58 8	7.5-57 30	
Baikal ⁵	=	-	24-48 -	-
Swedish lakes ⁶	(1972)	3.8 5.0 7.1		4.4-4.9 5.0-5.9 6.0-7.0

¹this study

² Patalas (1971)

³Sprules (1975)

⁴Ravera (1969)

⁵Kozhov (1963 <u>in</u> Schindler and Novén 1971)

⁶ Almer <u>et al</u> (1974)

Although some evidence for reduced carbon uptake in acidic lakes exists (Kwiatkowski and Roff 1976), Clearwater Lake does not fit the hypothesis of Grahn $\underline{\text{et}}$ al (1974) that acidification leads to reduced production.

The zooplankton community in Clearwater Lake was impoverished in species number as were other acid lakes in our study area and in other parts of the world (Table 8). Dominance of the acid tolerant cladoceran (De Costa 1975) Bosmina longirostris was evident. Chydorus sphaericus was present in most collections but contributed less significantly to total biomass. In near neutral, oligotrophic lakes morphometrically similar to Clearwater lake, Patalas (1971) reported co-dominance by a cyclopoid and a diaptomid. Zooplankton biomass was reduced (Table 8) in comparison to values reported by Ravera (1969) and Kozhov (1963 in Schindler and Novén 1971) for non-acidic oligotrophic lakes.

It is well documented that zooplankton grazing can affect phytoplankton biomass (Shapiro et al 1975) and production (Hargrave and Geen 1970). The efficiency with which zooplankton graze the phytoplankton is influenced by the size of the zooplankters - smaller forms graze less efficiently (Burns 1968) - and by the size of individual phytoplankters - larger forms are grazed less efficiently (Porter 1973). The dominant herbivorous zooplankton in Clearwater Lake, B. longirostris and C. sphaericus, are small (Yan et al unpub. studies) and probably do not efficiently graze on P. inconspicuum even though with a diameter of about 20 µm it is small for a dinoflagellate (Porter 1973). Thus, reduced zooplankton community biomass may be related directly to the change in phytoplankton community structure in Clearwater Lake.

In summary, Clearwater Lake is a clear, dimictic, well oxygenated lake with nutrient levels typical of oligotrophic lakes on the Precambrian

Shield. Chemically, the lake can be characterized by its low pH, elevated SO₄, Ca, Mg, Na and K levels and lakewater and sediment concentrations of Cu, Ni, Zn, Mn and Al that are at least an order of magnitude higher than in circumneutral lakes. The high H⁺ and metal concentrations have reduced the zooplankton and aerobic heterotrophic bacterial biomasses but have not altered the phytoplankton standing stock or production. The community structure of the phytoplankton and zooplankton is substantially different from that of circumneutral, oligotrophic lakes.

ii) Effects of base additions

In an attempt to determine what will happen in these acidified lakes when pH increases are induced either by a so-called reclamation procedure or, hopefully, through decreased inputs of acidic materials we have experimented with the addition of neutralizing materials to several of these lakes.

The neutralizing agents chosen were $Ca(OH)_2$ and $CaCO_3$ because they can effect an increase in pH with a minimum of other changes in lakewater chemistry (Grahn and Hultberg 1975). The acid-base reactions following additions are summarized in Pearson and McDonnell (1975).

Treatment of Lohi, Middle and Hannah Lakes (Table 9) initially raised lake pH to between 7 and 8 (Fig. 12). The pH decreased rapidly to about 7 as equilibrium was reached (Grahn and Hultberg 1975). Middle Lake and Hannah Lake have remained near neutrality since initial base additions despite continued H⁺ inputs from the atmosphere and runoff. However, Lohi Lake pH decreased steadily, necessitating a second addition of base in 1974. The pH declined, although at a more gradual rate, even after a third treatment in 1975. The reasons for this are twofold. Lohi Lake probably received more acid input than either Middle Lake or Hannah Lake because it drains a larger

Table 9. Additions of $Ca(OH)_2$ ($\mu eq~1^{-1}$) and $CaCO_3$ ($\mu eq~1^{-1}$) to study lakes.

Lake				Base a	dditions i	n μeq 1 ⁻¹				
	19	73	19		19	- T	19	76	Tot	al
	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃
Middle	380	190	-	-	-	_	-	-	380	190
łannah	-	-	-	-	360	155	-	-	360	155
.ohi	160	+	36	-	44	98	-	-	240	98
Clearwater	-	-	-	*	-	-	-	-	-	-
Welson	-	-	-	1-	37	18	13	10	50	28

- 20

watershed (Table 3) containing acidic Clearwater Lake. Secondly, base additions on a volumetric basis to Lohi Lake were less than those received by Middle Lake or Hannah Lake.

Base additions reduced Cu, Ni and Al levels (Fig. 13) substantially, probably by a precipitation mechanism. To a lesser extent Zn, Mn and Fe levels were also reduced. In Middle Lake for example, Zn levels dropped from 100 μ g 1⁻¹ to 25-50 μ g 1⁻¹, Mn from 350 μ g 1⁻¹ to 150-200 μ g 1⁻¹ and Fe from 150 μ g 1⁻¹ to 75-150 μ g 1⁻¹. As continued atmospheric inputs of Cu and Ni have not substantially raised lakewater concentrations in the three years since base additions, it is likely that levels are controlled by lake pH.

Although no pretreatment data on free metals exist, a comparison of 1976 data from Hannah Lake and Clearwater Lake show that base additions probably lowered free Cu and free Zn levels. Prior to treatment, total Cu and Zn levels in Hannah Lake were almost an order of magnitude higher than in Clearwater Lake with both metals mostly in the free state at the low pH. After base additions to Hannah Lake, free Cu (27 μ g l⁻¹) and free Zn (23 μ g l⁻¹) were lower than in Clearwater Lake (64 μ g l⁻¹ Cu, 38 μ g l⁻¹ Zn).

Several studies (Waters 1956, Hasler \underline{et} al 1951, Ahl \underline{et} al 1969 \underline{in} Wilander and Ahl 1972) have shown that nutrient levels, particularly phosphorus, increased after base additions. We found no change in phosphorus (Fig. 14) in any of the treated lakes.

Additions of base decreased Secchi transparency in all lakes, possibly resulting in thermal stratification occurring at shallower depths in Middle Lake and Lohi Lake. The greatest change occurred in Middle Lake, mean summer Secchi depth decreasing from 11 m in 1973 to 3.0 m in 1974. Prior to treatment, the lake was homothermous but in 1974, the metalimnion formed

at 9 m to 11 m in midsummer. Bottom water oxygen levels were not affected by base additions, remaining about 7 mg 1⁻¹ throughout the stratified period. In all cases, base additions increased the standing stocks of aerobic heterotrophic bacteria, and altered the type of microflora present. The heterotrophic-aciduric bacterial ratio (Table 10) increased after base additions (Thompson and Croll 1974). Thus, rates of detrital decomposition, known to be retarded in some acidic lakes (Leivestad et al 1976), could have increased. There is, however, indirect evidence that rates of decomposition had not been reduced by acidification in the recent past in Clearwater or Lohi Lakes. Sediment pH increased with depth from 4.0 to 5.5 in the top 12 cm of sediment. However, organic content (as percent loss on ignition) remained approximately constant with depth at about 16 to 25%.

Massive reductions in phytoplankton biomass were observed in Middle, Hannah and Lohi Lakes immediately after base additions (Fig. 15). Lesser base additions, effecting smaller changes in lake pH, (0.8 units in Lohi Lake in 1974, 0.9 units in Nelson Lake in 1975 and 1976) did not cause such reductions.

Within a few months, phytoplankton biomass increased to, but in no case exceeded pre-addition levels. As biomass was better correlated with phosphorus than with pH (Fig. 10) and as base additions did not alter phosphorus levels, this result was reasonable.

Phytoplankton species composition of the lakes with initial pH <4.7 was altered by base additions (Fig. 16). Dominance shifted from dinoflagellates to the chrysomonads more typically observed in circumneutral lakes (Schindler and Holmgren 1971). Thus, changes in algal community structure induced by acidification are reversible.

Table 10. Mean lake pH and ratio of aerobic heterotrophic bacteria to aciduric bacteria in study lakes in 1974.

Lake	l m. below lake surface	1 m. above lake bottom	mean pH
Hannah	0.27	0.18	4.3
Middle	184	20.3	7.0
Clearwater	0.18	0.28	4.2
Lohi	136	26.3	6.2

In all cases where base additions raised the lake pH from circa 4.5 to neutrality, zooplankton standing stocks were immediately and substantially reduced (eg. Fig. 17). As with phytoplankton, additions resulting in smaller pH elevations did not affect zooplankton biomass.

Crustacean zooplankton communities, unlike the microbial and phytoplankton communities, have not yet changed to those resembling circumneutral oligotrophic lakes. The delay in zooplankton response is not surprising in light of their longer generation times and the complete absence of many species typical of oligotrophic lakes. Although biomass ultimately returned to pre-addition levels (Fig. 17), re-establishment of typical, non acid-stressed community composition must await the recolonization of the lake by several species.

The reduction in standing stocks of zooplankton which would preferentially graze chrysomonads over dinoflagellates (Porter 1973) may partially explain the return to dominance of the chrysomonads after base additions. Other factors are their efficient utilization of phosphorus at low concentrations and their rapid doubling time (1-2 days, Lehman 1976) compared to that of the dinoflagellates (3-4 days, Von Stosch 1973).

iii) Effects of phosphorus additions

Although the phytoplankton community biomass did not increase after base additions (Fig. 10a), increases were observed after small additions of phosphorus (Fig. 10b). Fertilization of Middle Lake with phosphoric acid raised total phosphorus levels from between 2 and 5, to 8 mgm⁻³ in 1975 and to 13 mgm⁻³ in 1976. Concentrations in Hannah lake were raised to 11 mgm⁻³ in 1976, an increase of 7 mgm⁻³ over 1975 levels. These relatively small additions induced substantial and significant (p <0.005) increases in mean phytoplankton biomass (Fig. 15).

Additions of base induced reductions in the relative importance of the inorganic fraction of nitrogen (Table 11). Additions of phosphorus, however, caused much more substantial reductions in total nitrogen content of the water, either because of increased uptake and reduction by phytoplankton or increased rates of denitrification. The proportion of nitrogen occurring in inorganic forms decreased much more rapidly than when base alone was added.

The additon of phosphorus effected changes in phytoplankton species composition of a different nature than those induced by base additions. Blue-green biomass increased in all cases, an observation that is at variance with the theory of Shapiro (1973) since the pH never exceeded 7.0. Blue-greens, in fact, formed virtually all of the phytoplankton biomass in Middle Lake in 1975 after phosphorus was added. In 1976, in contrast, green algae were most often dominant after fertilization. Fertilization of Hannah Lake in 1976 caused increases in biomass, but not in the structure of the community, previously dominated by chrysomonads, and to a lesser extent by green algae.

Whole lake fertilization experiments have had diverse effects on phytoplankton community structure. Shifts to communities dominated by chrysophytes (Langford 1948), byblue-greens (Smith 1969) and by different groups in different years of fertilization (Schindler et al 1973) have been recorded. Since the occurrence and seasonal periodicity of different classes of phytoplankton are not solely governed by nutrient levels (Round 1971, Hutchinson 1967) the diversity of responses observed in our studies is not remarkable. It is evident, however, that small changes in phosphorus concentrations can have marked effects on the planktonic primary

Table 11. Total nitrogen (TN) and total inorganic nitrogen (TIN) in treated lakes.

Lake	Year	Treatment	TN (mg	m ⁻³)	TIN/TN (%)
Middle	1973	none	610	460	75
	1973-74	base additions	667	482	72
	1975	P additions	485	255	53
	1976	P additions	469	175	37
Hannah	1973	none	900	780	87
	1974	none	720	590	82
	1975	base additions	810	590	73
	1976	P additions	530	250	47
Lohi	1973	none	304	180	59
	1974	base additions	195	97	50
	1975	base additions	252	81	32
	1976	none	202	69	34

producers.

Two factors complicate the interpretation of zooplankton biomass data as it relates to base and phosphorus additions: 1) the mean annual zooplankton biomass in untreated Clearwater Lake varied by as much as threefold (Table 12). 2) The recovery of zooplankton biomass to preaddition levels in base-treated Lohi Lake occurred the 3rd summer after treatment (Fig. 17), but phosphorus additions followed base additions by 1 and 2 summers in Hannah and Middle Lakes respectively.

Changes in zooplankton biomass and community structure from 1973 to 1976, were quite similar in Middle and Lohi Lakes, despite the fertilization of the former. As phytoplankton biomass had increased in response to fertilization in 1975, zooplankton biomass might have been expected to increase as well. Most of the phytoplankton biomass, however, was contributed by the filamentous blue-green, Mastigocladus, a species probably not preferred as a food source by grazing zooplankton (Porter 1973, Arnold 1971). Zooplankton biomass increased to levels approximating pretreatment levels in Middle and Lohi Lakes by 1976. Community structure had not been influenced by the treatments (Table 12).

The pattern in Hannah Lake has been quite different, although reasons for the difference are elusive. Pretreatment zooplankton standing stocks were much lower than in all other study lakes (Table 12), and while cladocera were the most important community component, as in the other lakes, immature copepods contributed significantly to total biomass (Table 12). The biomass of nauplii and cyclopoid copepopids increased markedly after fertilization. The community of Middle Lake had remained cladoceran dominated after similar treatments.

Table 12. Crustacean biomass and percent composition in study lakes before and after treatment.

Lake		Total Crustacea ¹ mg m ⁻³ dry weight	Pe cladocera	rcent of cyclo- poida	mean biom cala- noida	nass nauplii
Middle	1973	9.0	93	2	0	5
	1974	0.8	19	66	11	5 4 31
	1975	1.4	16	53	0	31
	1976	16.1	97	2	0	1
Hannah	1973	0.6	70	7	0	23
	1974	0.8	40	34	25	1
	1975	0.1	11	36		53
	1976	30	5	37	0 0	58
Lohi	1973	19.9	81	7	0	12
	1974	1.3	77	17	6	0
	1975	0.7	45	36	6 0	19
	1976	8.1	79	14	0	7
Clearwater	1973	5.3	89	5	0	6
	1974	14.1	96	4	Õ	Õ
	1975	4.6	83	12	Õ	0 5
	1976	9.7	75	11	Ö	14

¹Monthly weighted averages of 12 to 24 collections, each of which was combined over 4 stations at each sampling depth and volume weighted with depth.

SUMMARY

Annual emission of SO_2 and H_2SO_4 from the nickel smelters at Sudbury averaged $\sim 2 \times 10^6$ mt yr⁻¹ over the past 25 years, resulting in acidification of a great number of lakes in an area of >5000 km². The bulk samples collected in the Sudbury area were acidic and is associated with excessive deposition of Cu, Ni, Zn and Fe, resulting in elevation of heavy metal concentrations in numerous lakes and streams. Acidic precipitation and slight elevations in lake water metal concentrations have been documented recently over a large part of south-central Ontario. Because the bedrock and overburden of a major portion of eastern Canada can provide very little buffering capacity, eventual acidification of thousands of lakes is inevitable if precipitation acidity remains high.

The major ion content of acidic lakes is substantially altered; SO₄, Ca, Mg, Na and K concentrations are elevated relative to unaffected Precambrian Shield Lakes. Because of the low pH, a major portion of the heavy metals are in the "free" or ionic form. Phosphorus and nitrogen levels are, however, typical of oligotrophic Precambrian lakes.

The biology of an acidic lake is less atypical than previously believed. Phytoplankton biomass and productivity were similar to those of circumneutral Precambrian lakes, and were related to phosphorus concentration rather than to pH. Species composition was drastically altered with dinoflagellates, especially Peridinium inconspicuum, rather than chrysomonads dominating. Zooplankton biomass was reduced and community composition altered such that the acid-tolerant cladoceran Bosmina longirostris dominated.

The addition of base $(Ca(OH)_2/CaCO_3)$ to acidic lakes raised the pH and lowered the heavy metal concentrations but did not affect the nutrient

levels. The composition of the microflora was altered such that heterotrophic bacteria were much more important relative to aciduric types. The phytoplankton biomass was initially drastically reduced, but increased to pretreatment levels within months. Species composition returned to that typical for an oligotrophic Precambrian lake. Zooplankton standing stocks were substantially reduced by treatment. Biomass ultimately returned to pre-addition levels, but community composition was unaltered after 3 years.

Fertilization of 2 lakes with low levels of phosphorus (increases of 5-7 mg m⁻³) had pronounced effects on phytoplankton biomass and species composition. Although changes in species composition were not completely reproducible, blue-green biomass increased in all cases although lake pH remained at or below 7.0. Zooplankton biomass increased, although by no more than in an unfertilized, neutralized lake. Composition was again not altered.

The changes that acidification and heavy metal contamination had brought about in these lakes were, therefore, at least partially reversible. The rate at which biotic components reverted to communities typical of oligotrophic Precambrian lakes decreased with generation time such that after 3 years the zooplankton populations remained atypical.

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LIST OF FIGURES

- Fig. 1. SO₂ emissions from Sudbury for 1967-76. Dotted line represents emissions from single largest smelter, with post-1972 output from a single 381 m tall stack. Emissions from a number of large centres are included for comparison (Acres Consulting Services Ltd. 1975).
- pH of bulk precipitation collections in southern Ontario. Under-Fig. 2. lined figures are from Kramer (1976a) for 1970-75, others are for 1976. Areas with large dots are regions of calcareous Paleozoic bedrock.
- Fig. 3. Possible extent of acidification of freshwater in eastern Canada (data from Kramer 1976c, Ryder 1964). Calcareous regions are not susceptible to prolonged acid loadings; the very susceptible areas have many localized regions (clay plains, moraines, etc.) capable of providing adequate buffering capacity in small isolated regions.
- a. pH of lakes in the Sudbury region. Shaded portions represent Fig. 4. areas where most lakes have pH <5.5, and include $\sim 5300~\rm km^2$. b. SO, levels in surface waters (g m $^{-3}$).

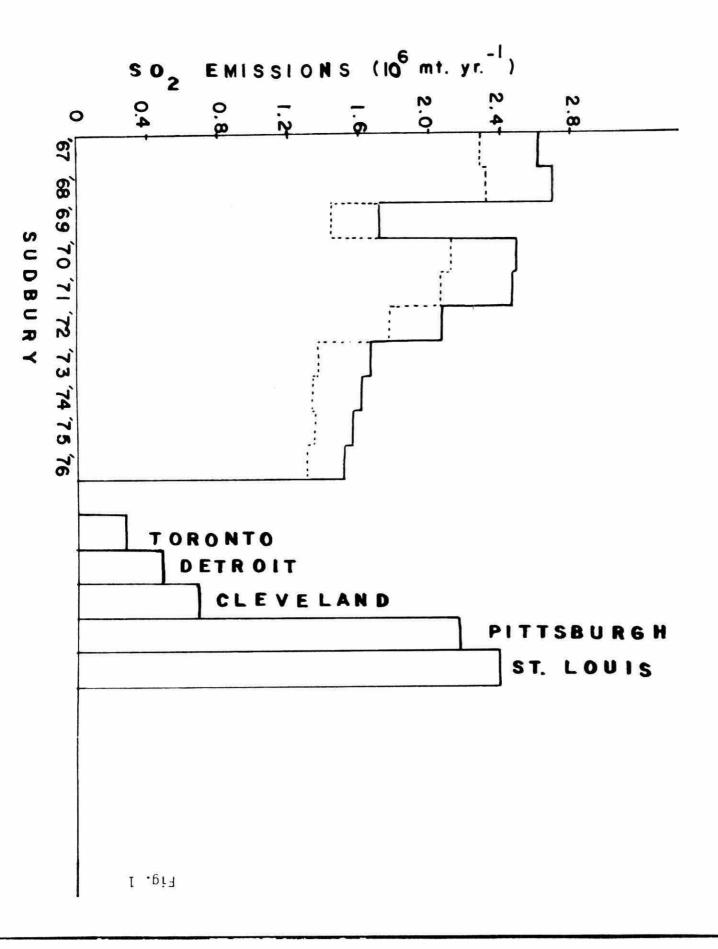
c. Wind rose for Sudbury (1956-66).

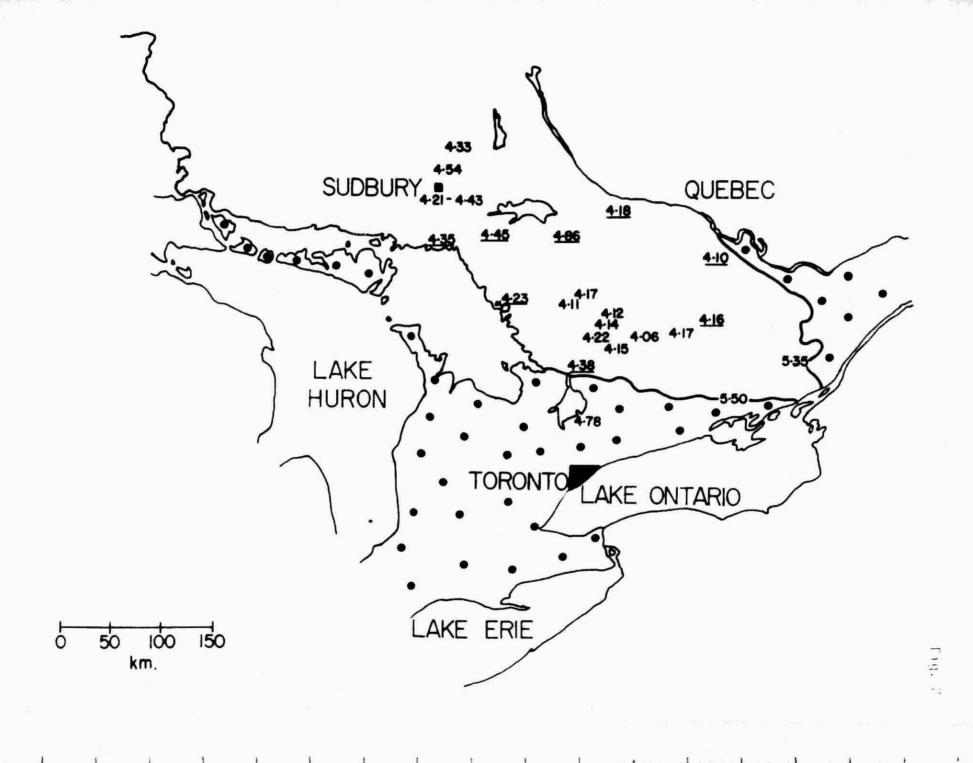
- d. Salmonid fisheries status for study lakes. pH <5.5 line is superimposed.
- e. Status of trout populations in the study lakes related to pH.
- a. Distribution of surface water nickel concentrations (mg m^{-3}) in Fig. 5. the study lakes.

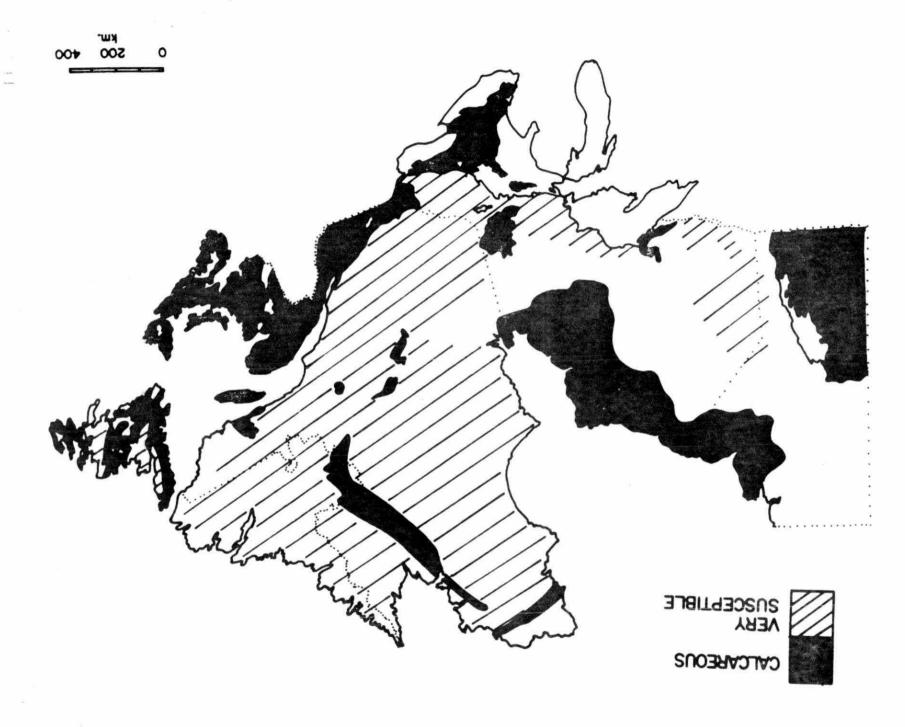
b. Distribution of sediment nickel concentrations ($\mu g/g$ of dry sediment) in the study lakes.

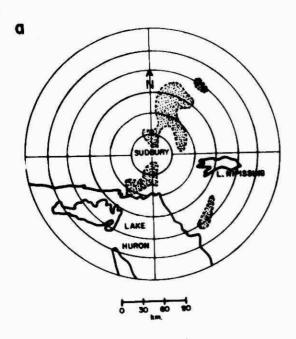
- c. Distribution of surface water copper concentrations (mg m^{-3}) in the study lakes.
- d. Distribution of sediment copper concentrations ($\mu g/g$ of dry sediment) in the study lakes.
- Location of 4 major study lakes. H = Hannah, M = Middle, L = Lohi, Fig. 6. C = Clearwater. Heavy line delineates watershed area.
- Profiles of pH, Ni and Cu in Clearwater Lake sediments at 3 Fig. 7. different stations.
- Volume-weighted whole-lake nitrogen concentrations in Clearwater Fig. 8. Lake. TIN = total inorganic nitrogen = $NO_2 + NO_3 + NH_3$. TN = total nitrogen = TIN + organic nitrogen.

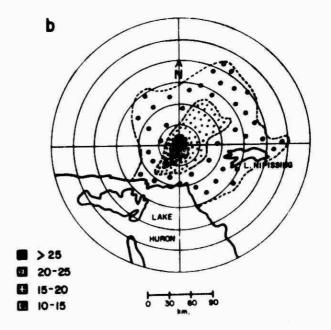
- Fig. 9. Phytoplankton composition in the euphotic zone (twice the Secchi disc depth) of Clearwater Lake.
- Fig. 10. Mean phytoplankton biomass vs. a) pH and b) total phosphorus concentration for Sudbury lakes with i) no treatment o ii) after base additions and iii) after base and P additions ■. Southcentral Ontario lakes are included △.
- Fig. 11. Primary production measured by the C¹⁴ technique in Blue Chalk Lake in south-central Ontario and Clearwater Lake.
- Fig. 12. pH vs time of 4 major study lakes. Treatments are denoted by: $\Delta = Ca(OH)_2$, $\triangle = Ca(OH)_2 + CaCO_3$, $\spadesuit = P$ additions.
- Fig. 13. Copper, nickel and aluminum levels in Middle Lake. Treatments are denoted by: $\triangle = Ca(OH)_2 + CaCO_3$, $\spadesuit = P$ additions.
- Fig. 14. Total phosphorus levels in Middle and Hannah Lakes. Treatments of Middle Lake are denoted by: $\triangle = Ca(OH)_2 + CaCO_3$, $\spadesuit = P$. Treatments of Hannah Lake are denoted by: $\triangle = Ca(OH)_2 + CaCO_3$, $\diamondsuit = P$.
- Fig. 15. Phytoplankton composition in Middle Lake. Treatments are denoted by: $A = Ca(OH)_2 + CaCO_3$, $\Phi = P$ additions.
- Fig. 16. Percent of total phytoplankton biomass contributed by:
 a) Chrysophyceae b) Dinophyceae. Each datum represents mean biomass of 15-26, separately enumerated samples collected between May and October of the year. Samples were volume-weighted composites of the euphotic zone.
- Fig. 17. Zooplankton biomass in Lohi Lake. Treatments are denoted by: \triangle + Ca(OH)₂ + CaCO₃, \triangle = Ca(OH)₂.

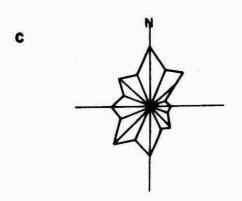


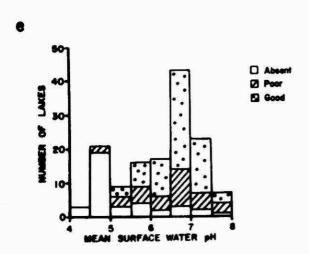


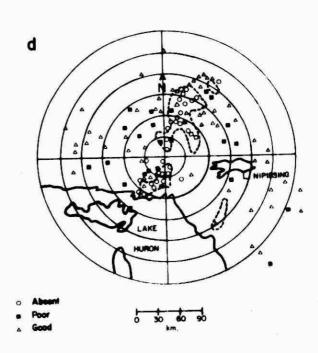


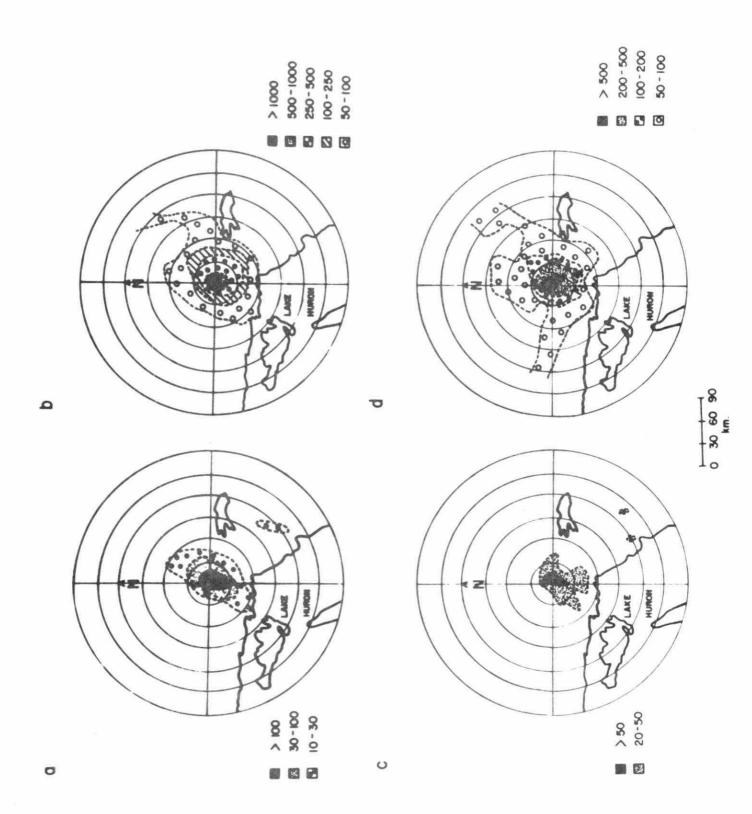












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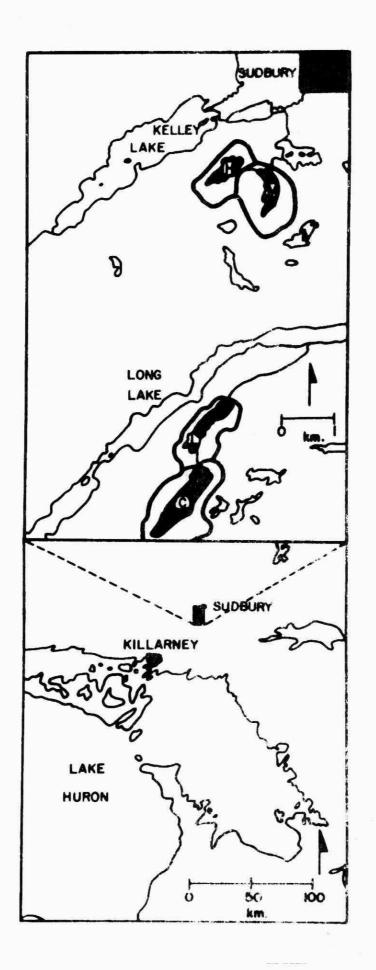
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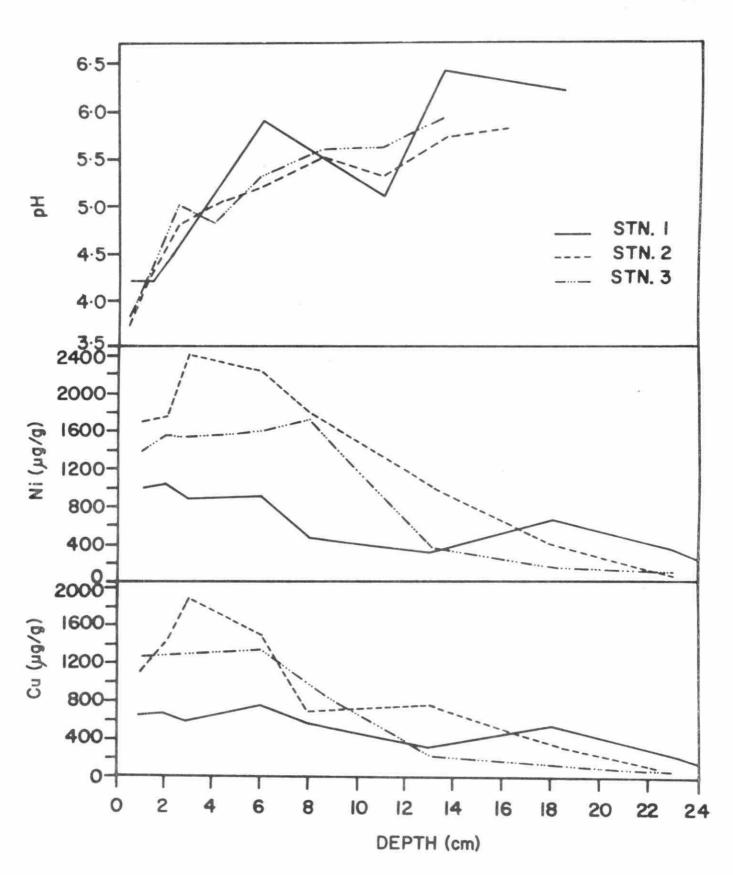
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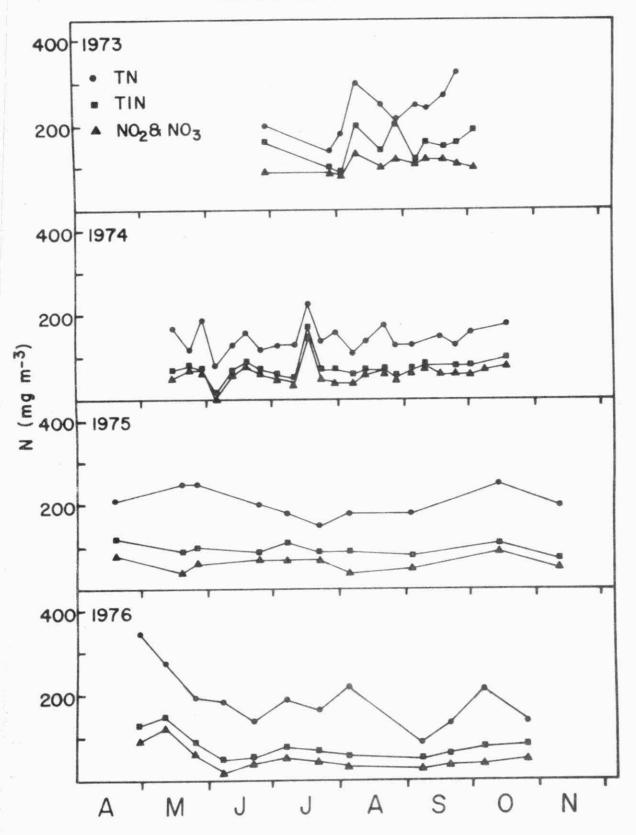
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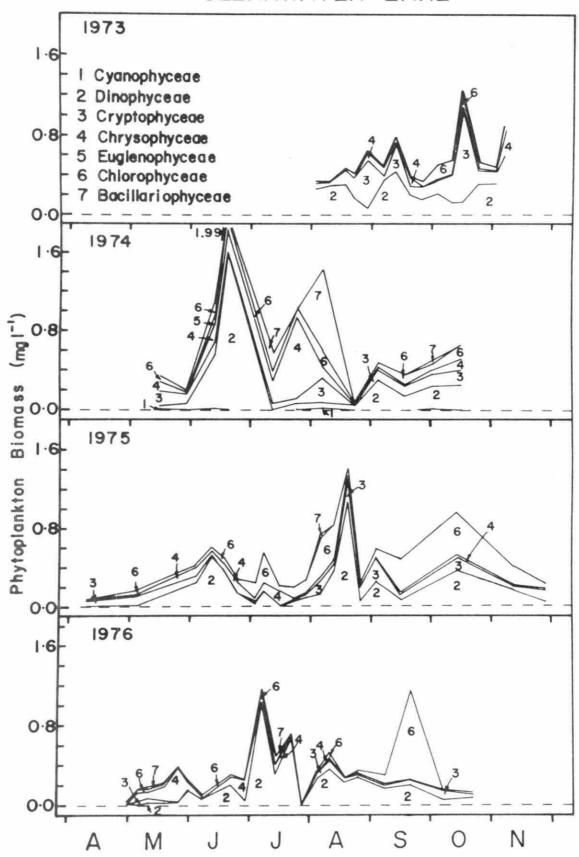


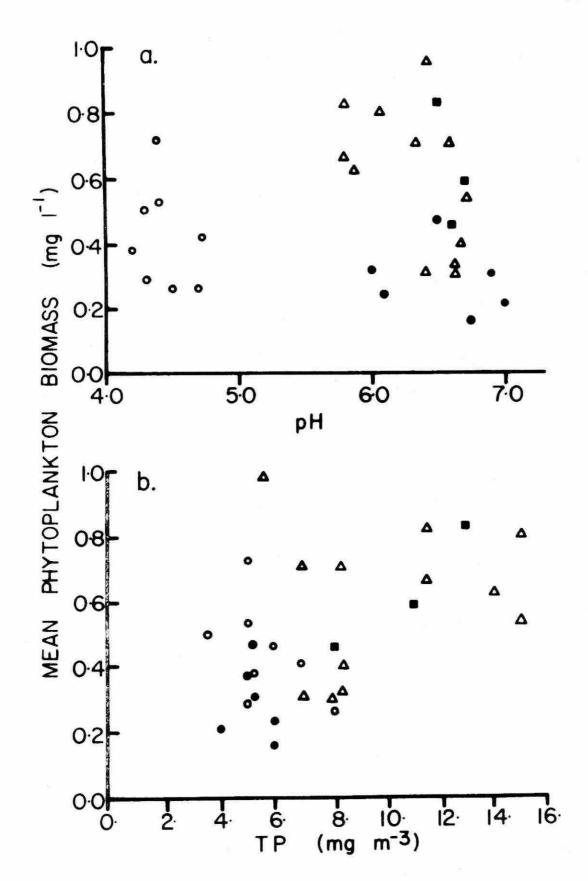


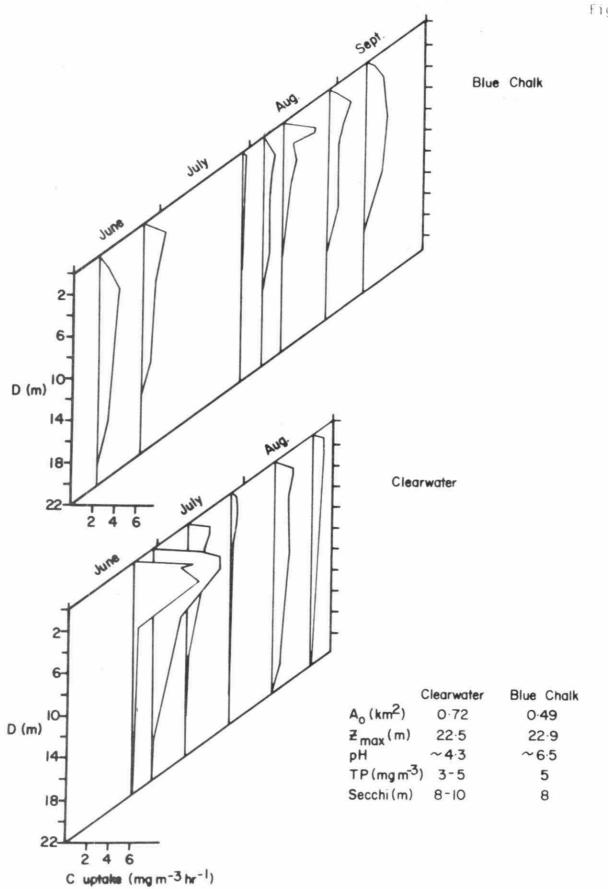
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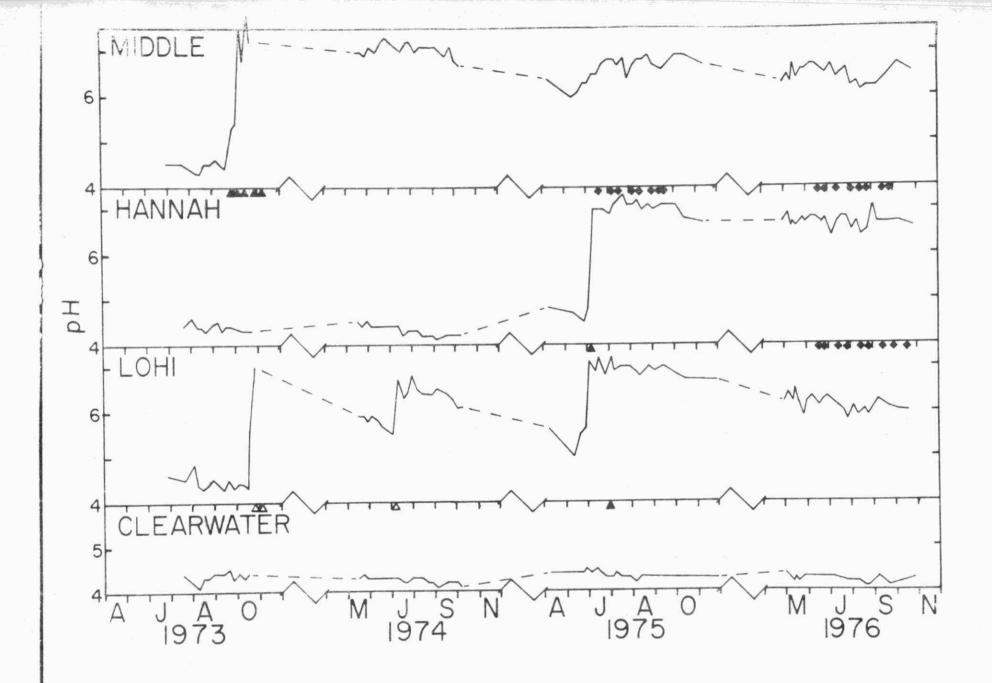


CLEARWATER LAKE

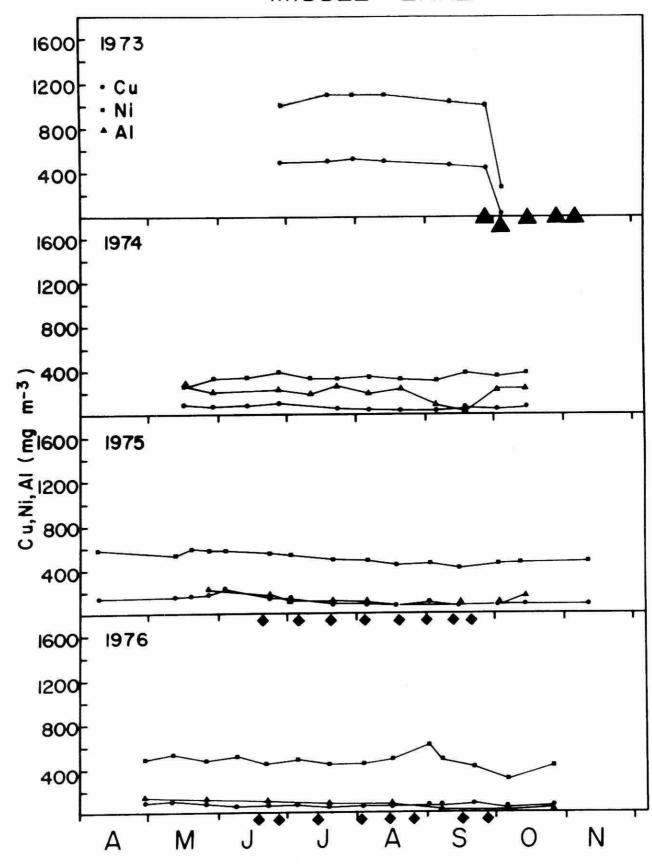




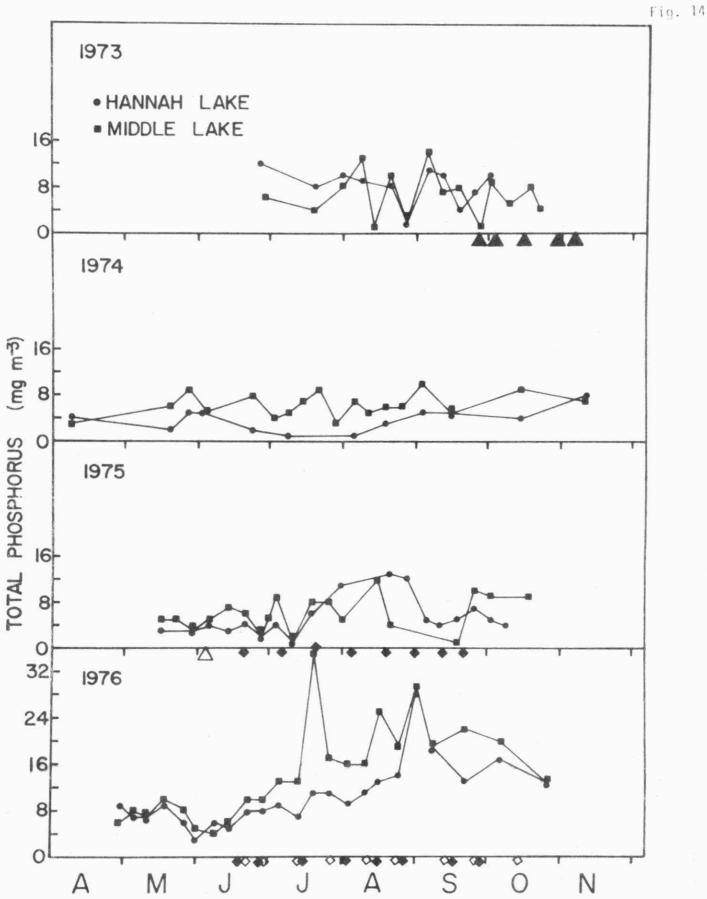




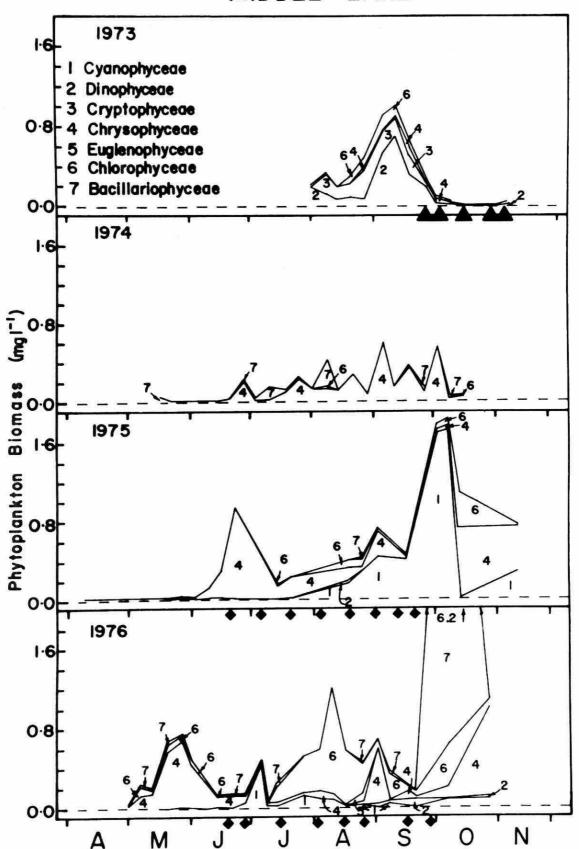


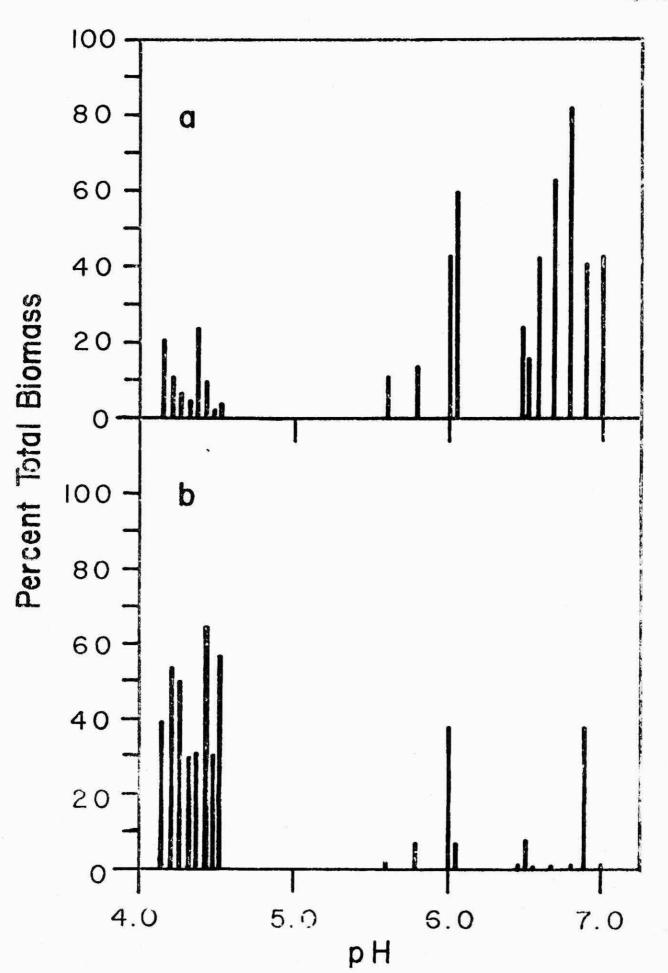


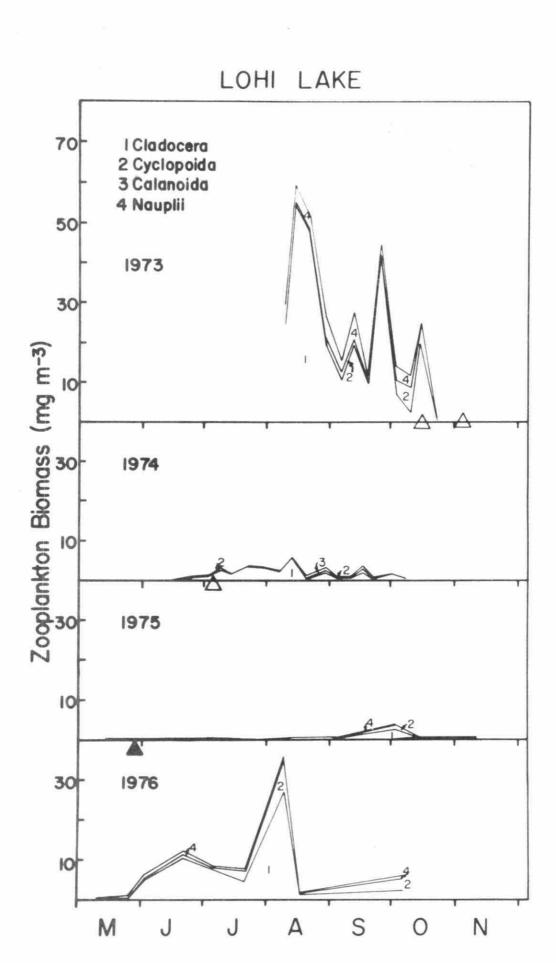




MIDDLE LAKE







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